WORK PLAN

Fluoride Survey Beginning with CY 2001

Sampling Specifications

[I] **Sample Location**

The Pocatello area would be sampled every two weeks within the industrial areas identified on the maps (Fig. 1 and 2). By May 15th of each year a list will be submitted to Simplot giving the following information:

1. Fifteen possible field locations for each area (designated on appropriate maps and selected from the 16 marked sites). The sampling sites will be divided into 5 categories depending on their distance from the emission source as follows:
   a. 0-1 miles
   b. 1-2 miles
   c. 2- 3 miles
   d. 4-5 miles

2. Names of field owners or leaseholders.

3. Contact people with telephone numbers for each field location.

In the event sites must be changed because of crops being grown other than forage crops, etc, an alternative site will be selected from the same site category (distance from the emission source).

[II] **Quantity and Frequency of Sampling**

Field sampling will be initiated during the growing season as determined by survey when 50% of fields have an average forage height over two inches. Sampling will be terminated when 50% of fields have an average height of forage growth less than two inches. The length of growing season will be determined for each area.

The growing period is expected to cover a four-month period, June though September. Specifications for this section are illustrated in the following table:

Area	# Samples/Area	Months Sampling	Sampling Frequency	Total Samples/ Area/Year
Pocatello	Target is 15	4	2/Month	120

[III] **Sample Collection Procedures**

Specific routes will be followed to collect samples. Routes will begin by collecting samples first from the areas most remote from the sources of fluoride, and followed by samples taken from areas increasing in proximity to avoid sample contamination.

Actual samples will be taken using the following procedure:

(a) After arriving at the desired field location, fields will be visually surveyed to determine if the average height of the forage is greater than two inches. If not, the field will not be sampled.

(b) If the average height of the forage is greater than 2 inches, the contact person (if available) will be notified before forage samples are taken.

(c) Notes will be kept in a logbook concerning the condition of the field.

(d) Samples will be taken using a "Z" pattern. Each sample shall consist of no less than10 clippings taken no less than 10 feet apart. Clippings comprising each sample should be of sufficient quantity to half fill a 3 gallon bucket.

(e) The forage sample in the container will be cut up until the maximum length is one inch and thoroughly mixed.

(f) The date and field on a lunch-sized paper bag will be noted. The bag will be half-filled with the clipped forage sample and folded shut.

(g) Left-over sample not to be analyzed will be discarded on the property from which it was taken.

NOTE: No samples will be taken from any forage less than two inches high.

Samples will be taken from standing forage.

Duplicates shall be taken from one-half of the samples in each area and held for nine months.

All results of sampling and analysis will be released to J. R. Simplot Company.

[IV] **Sampling Records**

A log containing the following information will be made of the field work:

(a) Date of Sampling,

(b) Field identification number,

(c) Field condition during sampling,

-Whether recently cut (no sample taken)

-Which cutting (1^{st}, 2^{nd}, 3^{rd}, if known)

-Whether healthy, heavy or sparse;

-Injury symptoms (pathogens. toxicity. nutritional)

(d) Is the field being grazed; and

(e) Is an alternative field being sampled (reason).

If most of the F is from deposition would not some be lost w/ all this grinding?

[V] Analytical Methods

For analyses of plant materials, samples are oven-dried in paper sacks at 80 C for at least 48 hours, finely ground in a Wiley mill and stored in a dry place until used.

A potentiometric method outlined by the Association of Official Analytical Chemists (Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC), Edit. K. Helrick, 15th Edition. pages 51- 56, 1990) will be followed in preparing the various forage samples for fluoride determinations and in making fluoride standard curves.
For analysis, one-fourth gram of a previously ground sample is placed in an acid-cleaned plastic beaker to which is added 1 milliliter (ml) of analytical grade acetone for wetting of the dry material. Most of the acetone is allowed to evaporate from the material in a fume hood.

Twenty ml of 0.05 N nitric acid solution is added. This mixture is stirred for at least 30 minutes with a magnetic stirrer, following which 20 ml of 1.1 N potassium hydroxide solution is added and stirred an additional 30 minutes. Next, 5 ml of 0.2 N nitric acid solution is added along with 5 ml of 0.4 M sodium citrate solution (pH 5.5), containing 1 part per million (ppm) fluoride. Samples are analyzed in duplicate using two different digests and 2 fluoride electrodes. If the analyses differ they are repeated. Standards are run at least daily using 0.1 to 10-ppm samples.

Periodically, to maintain quality control vegetation samples containing known fluoride concentrations are analyzed. Amounts of fluoride in each sample are calculated as ppm dry weight of plant material using the equation:

$$\text{ppm F (ug/g)} = \frac{(C - 0.1)\ 50}{W}$$

where:

C = ppm F from standard curve.
W = grams of sample used.
0.1 = ppm of F present in the sodium citrate solution.
50 = total ml of solution.

[VI] Description of Potentiometric Instrument and Standard Curve Determination

The potentiometric instrument is an Orion 720 A that measures directly into relative millivolts. Any units may be used for calibration. The direct measurement technique involves calibrating the 720 A with one to five standards of known concentration. Unknown sample concentrations are then read directly from the display in the concentration units used for calibration.

During calibration the most dilute standard should always be used first. The 720 A automatically recognizes slope direction. When 3 or more standards are used the instrument uses a point to point calibration scheme. When measuring in a particular region of the curve the electrode slope for that region is employed in the calibration of sample concentration. The electrode slope displayed after calibration is the average slope for all the segments of the entire calibration curve. Use of the scheme increases accuracy in the different regions of the calibration curve. Blank correction occurs automatically when three or more standard are used. The standards used for calibration do not need to include a blank.

Six standard solutions of fluoride will be used to determine the standard curve as follows: 10 ppm, 5 ppm, 2 ppm, 1 ppm, 0.5 ppm, and 0.2 ppm. Small plastic acid-washed containers will be used for the standard solutions. The standard solution will be placed into a plastic container containing a stirring bar. The electrode will be inserted into this solution about 12 mm and stirred magnetically. Relative mv readings will be noted at 3 minute intervals until the change is <0.2 mv/min. The electrodes are then removed, blotted lightly with absorbent paper, and repeated with 0.5, 1.0, 2.0, 5.0, and 10.0 ppm solutions. Two electrodes on two separate potentiometers are used for fluoride determination. A separate standard curve will be used for each electrode. Measurement in millivolts will be plotted against concentrations of standard solutions using semi-logarithmic 2 cycle paper.

The relationship between the Δ mv and the fluoride level is linear with a semi-logarithmic graph when the fluoride concentration range is between 0.02 – 10 ppm and the relative millivolts in the range of 80-200 units. If linear results are not obtained in this range, samples are remade and reanalyzed.

The co-efficient of variation in test results of Δ mv on each standard point (0.2, 0.5, 2.0, 5.0, and 10 ppm F) has been 2-3%.

[VII] Quality of Analysis and Control

(a) A sample blank will be prepared using procedures outlined previously for preparation of the plant material. Plant material will be used from an area remote from the fluoride emitting source containing low fluoride in the tissue. A known amount of fluoride will be added to the sample solution and percent of recovery determined.

(b) Spike materials will be used in order to assess percent recovery on one or more of the samples. The spike material will consist of the prepared plant sample to which a known amount of analyte (standard NaF) will be added. This should not be excessive in relation to the amount present (e.g., about 2x).

The analyte added should be in the same chemical form as present in the samples for accurate determination. The recovery rate of standard fluoride added to the sample with the fluoride electrode has been found to be 96.0-105.0% when measuring 20-100 ppm in the sample. Results of a spiked sample will be included with each analysis survey beginning with 2001.

6-6-01

FLOURIDE SAMPLES COLLECTION
(POCATELLO, IDAHO)

Trip Sample: From Logan.

A. Farm # 8. Elden Bybee (12388 N. Hawthorn). 1 Sample. Grass. – Flooded / Really wet

B. Farm # 6E. Floyd Johnson. East of Floyd's home. 1 sample. Pasture.

C. Farm # 6. Floyd Johnson. 1 sample. Pasture.

D. Farm # 5. Dean Williams. 2 samples East and West (5E, 5W). 1 **Duplicate** on **West Side**. Alfalfa.

E. Farm # 4. Randy Chandler. Grass. 1 sample **Front**. Irrigated/Flooded - not wet

F. Farm # 11. UP&L. Grass. 1 sample. – Real wet / flooded irrigated

G. Farm # 12. Rich Dixion. Alfalfa. 1 sample.

H. Farm # 3. Russel Reese. Grass. Divide the field and take **2** samples: **3N** and **3S**.

I. Farm # 7 Garth Turnipseed. Grass. 1 sample.

J. Farm # 2 Wiegel Payne. Grass. **2** samples: **2S** and **2N**.

K. Farm # 1 Rulon Gull. Alfalfa. Divide the field and take 2 samples: **1S** and **1N**. Take a duplicate on **South Side**.